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ISS/SIMS CHARACTERIZATION OF UV/O_3 CLEANED SURFACES

W. L. BAUN
MECHANICS AND SURFACE INTERACTIONS BRANCH
NONMETALLIC MATERIALS DIVISION

OCTOBER 1979

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When solids are irradiated with ultraviolet light from a low pressure mercury discharge tube (UV/O_3), a complex reaction involving interaction of both photons and ozone produces a cleaning action on the surface. In this work, the efficiency of the UV/O_3 method is evaluated using ISS and SIMS. The UV/O_3 method is found to be useful for both surface cleaning and storage following cleaning by conventional techniques.

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FOREWORD

This technical report was prepared by W. L. Baun, Mechanics and Surface Interactions Branch, Nonmetallic Materials Division, Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio. This work was initiated under Project 2419 "Nonmetallic and Composite Materials" and was administered by the Air Force Materials Laboratory. The Work Unit Monitor is Dr. T. W. Haas.

This report covers work carried on between July 1978 and August 1979.

The author wishes to acknowledge helpful discussions on cleaning and adhesive bonding with N. T. McDevitt.

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SECTION I
INTRODUCTION

Surface treatments sometimes do not leave the surface as clean as necessary for purposes such as thin film deposition, microelectronic encapsulation, or adhesive bonding. In addition, when surfaces are cleaned, there is a problem of keeping them clean until they are used or processed further.[1] Exposure to ultraviolet radiation, hereafter referred to UV/O_3, provides a highly effective cleaning method and serves as a viable storage technique to keep materials clean following final processing. This report shows ion scattering spectrometry (ISS) and secondary ion mass spectrometry (SIMS) data from several types of materials before and after exposure to UV/O_3.

SECTION II

EXPERIMENTAL

The primary characterization instrument used in this work was ISS/SIMS. The components for this dual method are seen in Figure 1. Both methods use a low energy ion beam (1-3 KeV) to probe the surface. The ISS (Commercial Model 520 ion scattering spectrometer, 3M co., St. Paul, MN) measures the energy loss when the probing ion scatters from the outermost atomic layer of the surface. The SIMS technique measures the mass spectrum of the sputtered ions which are removed from the surface by the primary ion beam. A three element energy filter and Model 100C quadrupole mass analyzer (Uthe International, Inc., Sunnyvale, CA) were used for SIMS analysis. Reviews of the ISS[2] and SIMS[3] methods have appeared in the literature.

The UV source was a low pressure mercury discharge tube generating primarily two wavelengths of interest, 184.9 nm and 253.7 nm. The 184.9 nm wavelength is important because it is absorbed by oxygen and it causes the generation of ozone.[4] The 253.7 nm radiation is not absorbed by oxygen, but it is absorbed by the most hydrocarbons. In addition, it is absorbed by ozone accounting for the destruction of ozone in the reaction. Therefore, when both of these wavelengths are present, ozone is continuously being formed and destroyed. An intermediate product of both the formation and destruction processes is atomic oxygen which is a very strong oxidizing agent.

SECTION III
RESULTS AND DISCUSSION

Vig and Lebus[4] have performed extensive experiments and provided an exhaustive review of the UV/O_3 cleaning method. They use the contact angle method and a very simple but highly sensitive test, the steam test, to deduce cleanliness of the surface. This wetting test is sensitive to extremely small amounts of hydrophobic contaminants on the surface. These authors devised experiments which allowed exposure of samples to the 253.7 nm radiation, the 184.9 nm radiation, and the ozone generated by the 184.9 nm radiation. Another system allowed the options of exposing samples to 253.7 nm ozone, 253.7 nm only, or to ozone only. They came to the conclusion that while both UV light without ozone and ozone with UV light can produce a very slow cleaning effect. The combination of short wavelength UV light plus ozone such as that produced by a quartz UV lamp produces a clean surface much faster.

Typical ISS-SIMS data is shown in Figure 2 for titanium 6 aluminum 4 vanadium (Ti6Al4V), as received. This sample has not been degreased or treated in any way. The ISS spectrum is very weak showing many elements and in particular, carbon. If carbon is observed under the experimental conditions used here, then there is a very high concentration of carbon on the surface. Numerous other elements are also seen in the spectrum which was recorded at only 5000 counts per second full scale. Large quantities of sodium and potassium and fluorine, apparently from the processing step, are observed in addition to the alloying constituents. Note the cluster spectra, the calcium fluoride ion CaF^+ which may indicate that the fluorine is tied up on the surface by calcium. Titanium is hardly visible in either the ISS or SIMS data. Figure 3 shows data from the same material cleaned under ultraviolet light. The ISS spectrum now shows primarily titanium and oxygen. Perhaps a very small amount of carbon still exists but upon cleaning for a longer period of time, all trace of carbon disappears. This ISS spectrum is taken on a full scale of 25,000 counts per second as compared to 5000 counts per second on the earlier as-received specimen. Note also the change in the SIMS data, where before titanium was barely visible, now it is very strong. The TiO^+ cluster spectra is very strong indicating a great deal of oxygen activity on the surface. Note also the appearance of O^+ and OH^+ in relation to the fluorine that had been present initially. The CaF^+ has disappeared and now cluster spectra CaO^+ and $CaOH^+$ appear in the spectrum. Notice also the dramatic decrease of the potassium positive ion yield on this surface compared to calcium, for instance; no explanation is offered for this apparent decrease. Perhaps a change in chemical state produced a large relative yield change.

2024 aluminum alloy also gives similar results. The ISS spectrum is weak in Figure 4 and a great deal of carbon exists. The major peak is that of magnesium because the final rolling treatment leaves the surface magnesium rich. Comparison of oxygen with MgO spectra indicate that in this spectrum, the oxygen is stronger than in MgO indicating that probably there are oxygen containing impurities on the surface. The SIMS spectra show relatively little sodium and potassium compared to the spectra shown for Ti6Al4V and large quantities of magnesium in relation to the aluminum on the surface. Although the hydrocarbons give rather weak positive ion spectra, some ions characteristic of hydrocarbons are shown in the low mass region in the CH_n^+ region. With only a short-term exposure under the UV light the specimen of 2024 aluminum alloy gave the ISS/SIMS data shown in Figure 5. Nearly all of the carbon has disappeared from the ISS spectrum. The spectrum now is taken at 25,000 counts per second as compared to the spectrum from the as-received material at 5000 counts per second. This large increase in intensity indicates that the surface is much cleaner and is about average for a freshly prepared aluminum oxide surface. The SIMS spectrum from this sample changes rapidly as the ion beam erodes the surface. This is rather unusual when using this ion (^3He) because so little material is removed with time. However, here spectrum 2 is taken only 2 minutes after spectrum 1. As can be seen, the yield is rather low in the first spectrum indicating perhaps some loose material at the surface, then as the ion beam erodes away the surface the magnesium rich layer increases rapidly. The exposure to UV light was approximately as efficient as commercial degreasing as shown in Figure 6 where ISS data and SIMS data are shown for 2024 aluminum exposed to the commercial product used for degreasing called "Dry Clean." The surface showing the best water break test was that of 2024 aluminum cleaned first with a commercial degreaser and then exposed to UV light (Figure 6). Figure 7 shows that the ISS and SIMS spectra are virtually identical to those from the earlier cleaned samples. This sample then simulates the storage of pre-cleaned specimens under UV. Under these conditions, the samples remained clean indefinitely.

While it is possible that the UV/O_3 technique can remove gross contaminants, the method is much more effective if it is preceded by cleaning by chemical or other methods. It was found in this work, as well as by Vig and Lebus,[4] that there are some contaminants which cannot be reduced to zero with the UV/O_3 method. Vig and Lebus suggest that this is possibly due to the fact that some contaminants contain inorganic salts which cannot be removed by photosensitized oxidation. They also point out that perhaps in some thick films the bulk could be transformed into a UV resistant film by the crosslinking action of the UV light which penetrates the surface. Some changes in organic materials are observed in the ISS and SIMS spectra. In Figure 8 the ISS/SIMS data are shown for bulk polypropylene. In Figure 9 data are shown for polypropylene exposed to UV/O_3. Changes in the spectra are subtle. There is an improvement in the ISS spectrum with UV exposure for some unknown reason and perhaps slightly more oxygen is seen on the surface, maybe indicating surface oxidation of the polypropylene. There is some change in the fragmentation pattern observed, but fundamentally it remains very similar. A change in the spectrum not depicted here is that the fragments in the polypropylene in the UV exposed sample continue out beyond mass 80 to 90, while in the unexposed polypropylene no appreciable intensity of higher mass numbers is seen beyond mass 70. The small changes in the cracking patterns may be indicative of bond breaking at the surface. It is possible that the increasing size of fragments may indicate some amount of crosslinking in the polymer.

SECTION IV
SAFETY HAZARDS

The author wishes to call to the attention of the reader the safety hazards associated with short wave UV light. Exposure to short wave UV can cause skin and eye injury within a short time. In the construction of a UV/O_3 box such as that shown by Maddox,[1] great care should be taken in the construction and consideration of safety aspects. If no automatic shutters or other protective devices are used, then proper clothing and eye protection should be worn to prevent skin and eye burns. Further safety hazard is ozone, a highly toxic gas. Because of the production and simultaneous annihilation in the reaction as described earlier, it is not certain just how much gaseous ozone is released into the air in a given cleaning period and perhaps this varies with the material that is being cleaned. Nevertheless, one should be careful not to exceed the OSHA standard levels which are 0.1 parts per million.

SECTION V
CONCLUSIONS

ISS and SIMS results have shown the UV/O_3 cleaning procedure to be extremely effective in removing many contaminants from surfaces. It is simple, dry, inexpensive and provides an excellent method for storage following cleaning procedures. In addition, it is quite possible that the surface itself is more receptive to encapsulation or adhesive bonding because of the photosensitized oxidation process which does the cleaning on the surface. It is possible that this produces an active surface from the dissociation of excited species on the surface. Most products are gaseous and desorb from the surface.

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2. T. M. Buck in "Methods of Surface Analysis," A. W. Czanderna, Ed., Elsevier, Amsterdam, 1975, pp. 75-102.

3. A. Benninghoven, Surf. Sci 53, 596 (1975).

4. J. R. Vig and J. W. LeBas, IEEE Trans. on Parts, Hybrids and Packaging Vol. PHP-12, No. 4, Dec. 1976.

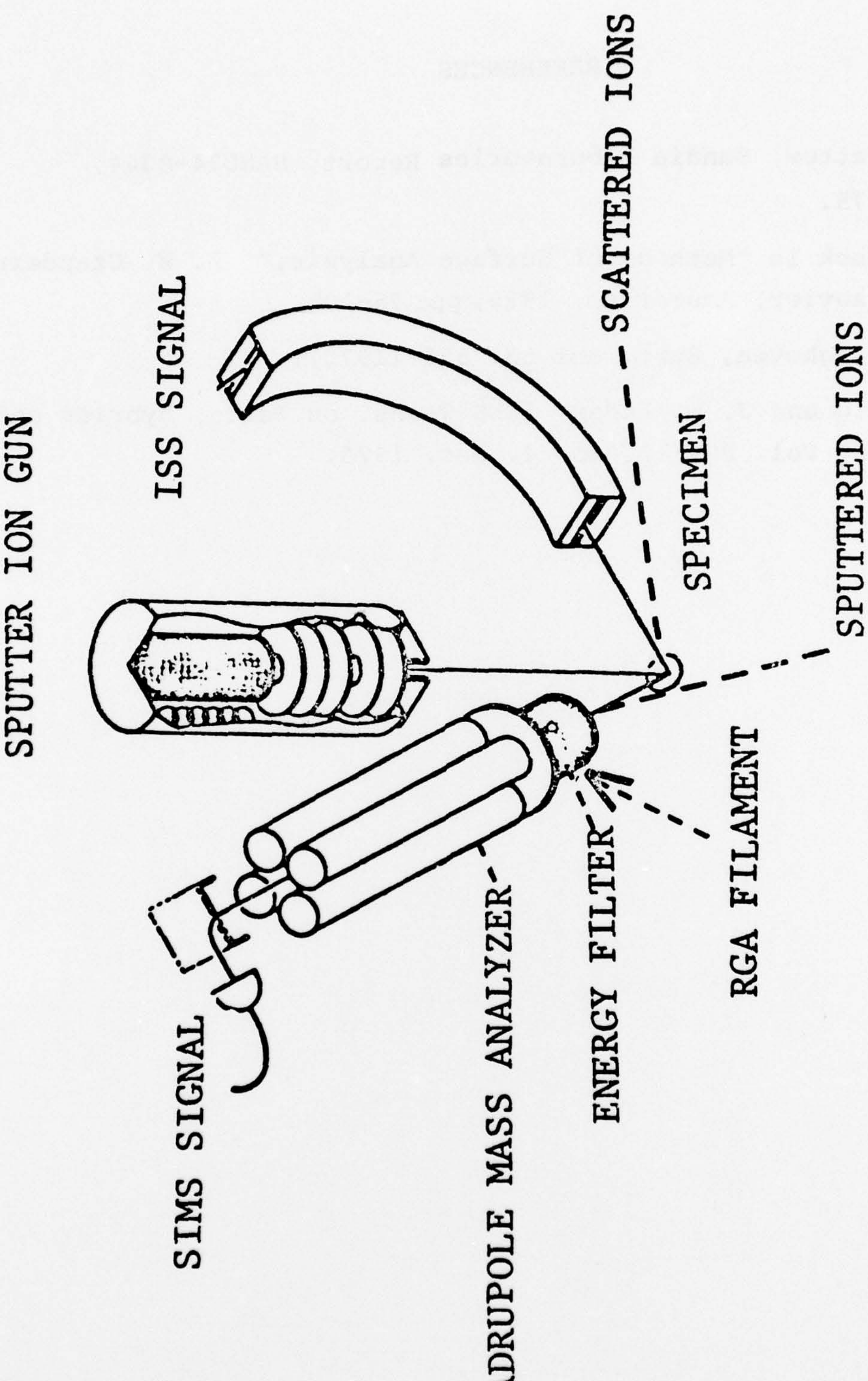

Figure 1. Components in UHV for ISS/SIMS.

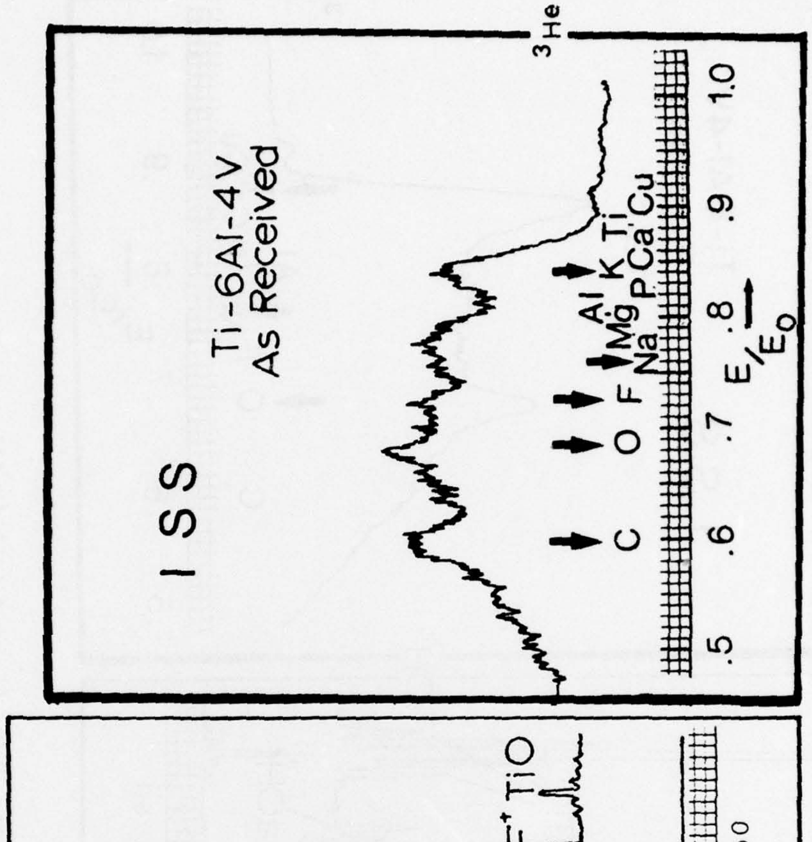

Figure 2. ISS/SIMS Data for Ti6Al4V Alloy as Received.

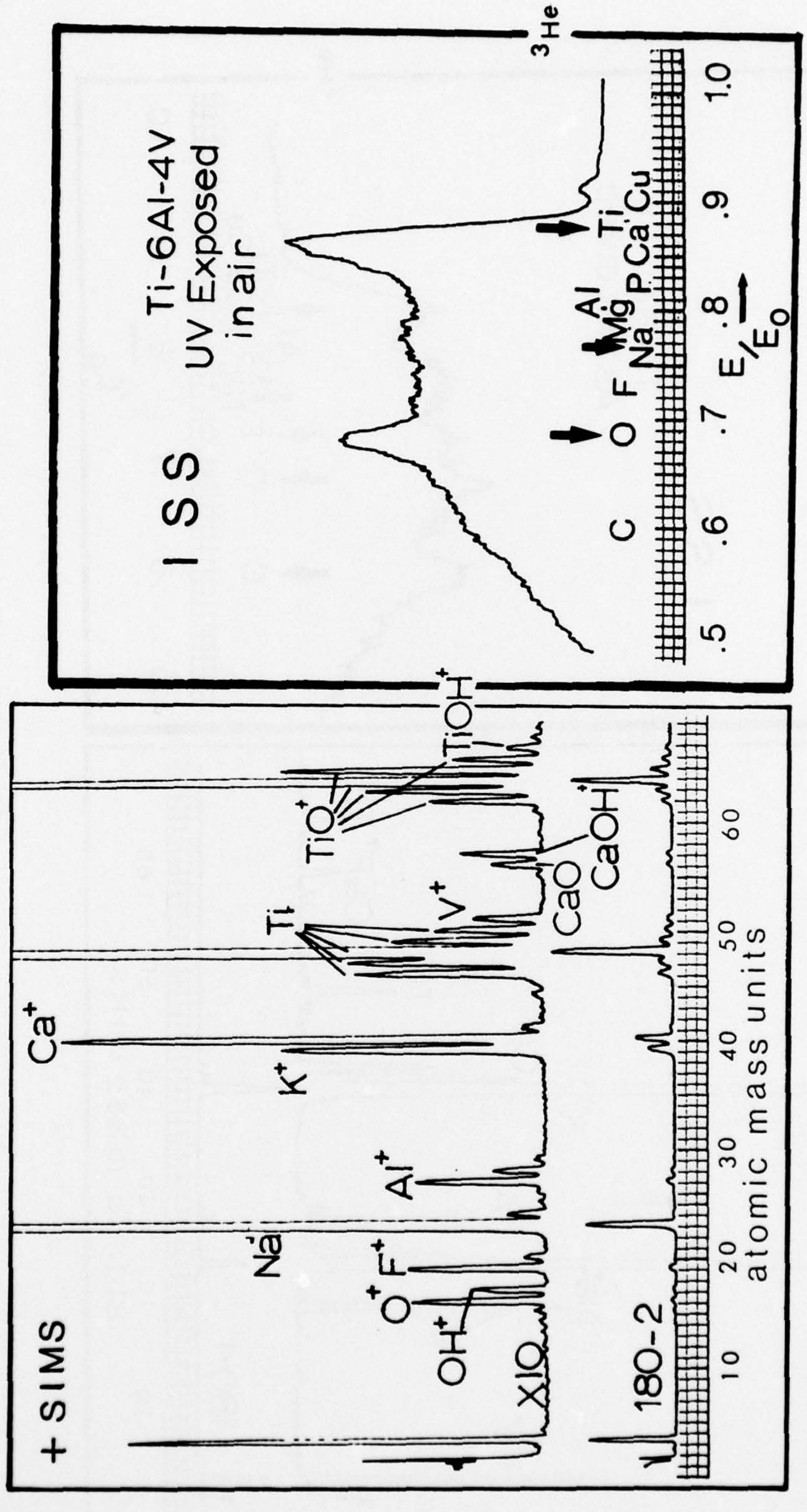

Figure 3. ISS/SIMS Data for UV/O_3 Cleaned Ti6Al4V Alloy.

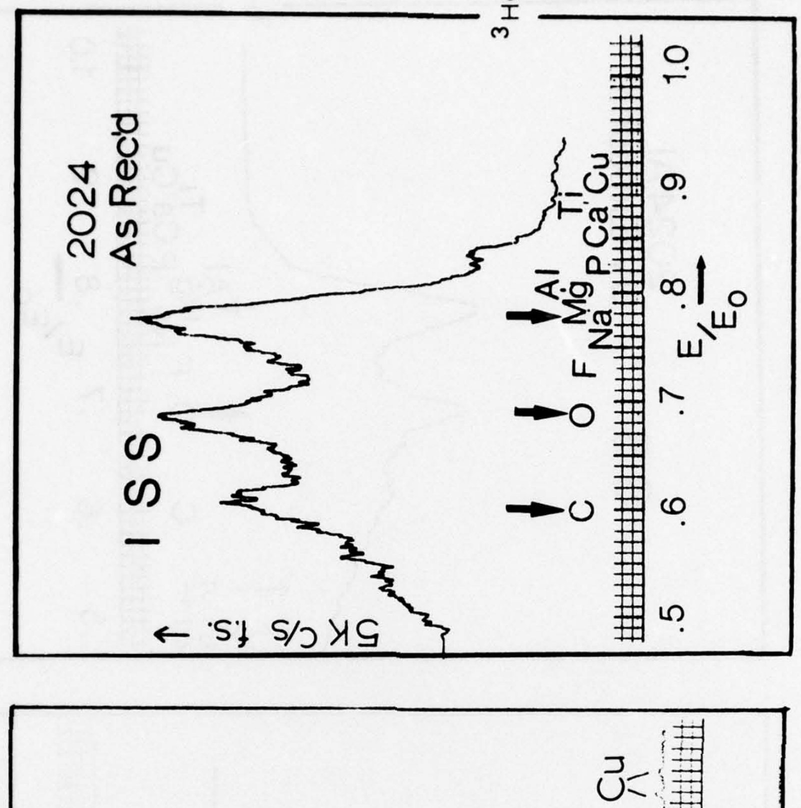

Figure 4. ISS/SIMS Data for 2024 Al Alloy as Received.

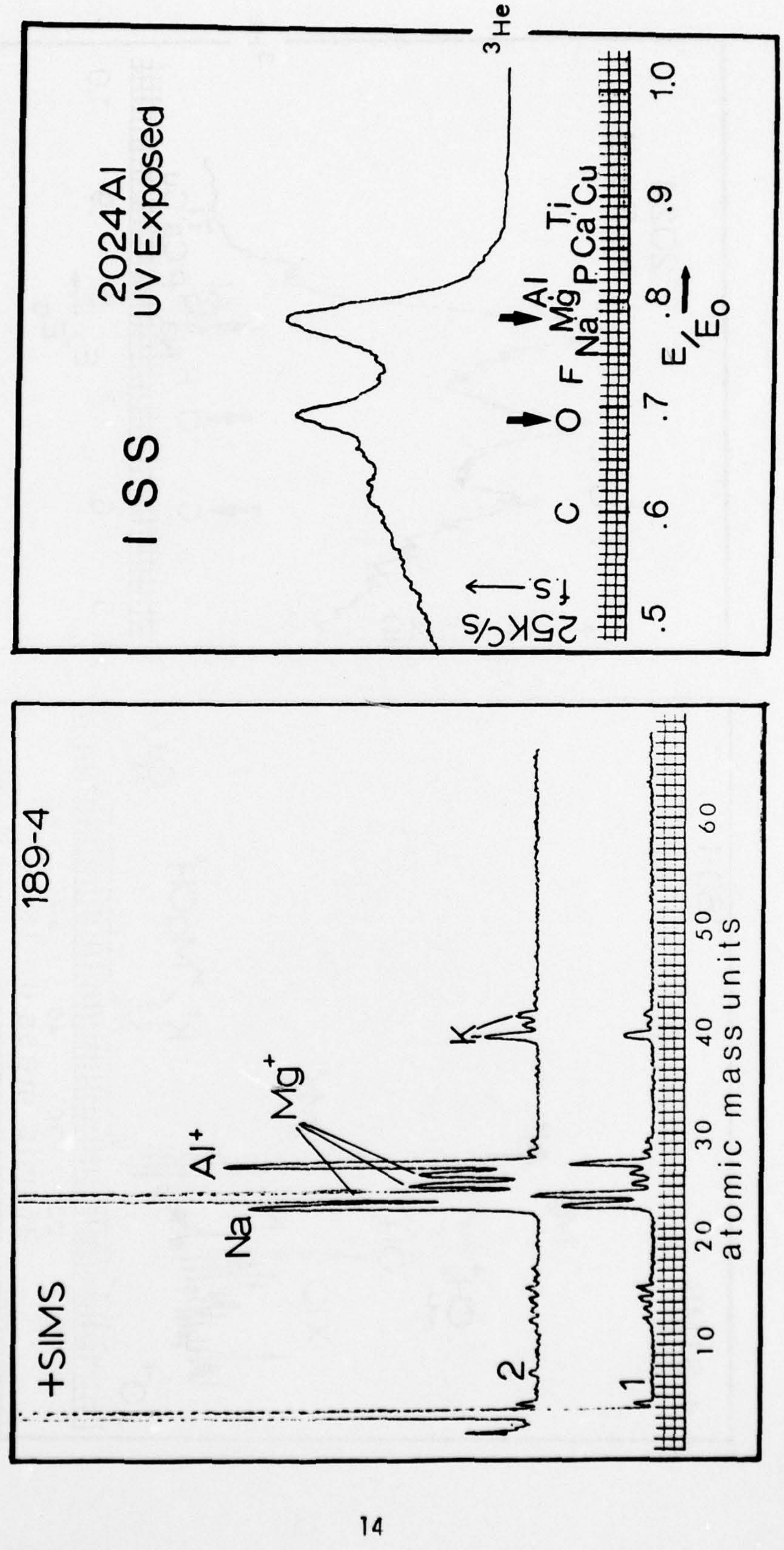

Figure 5. ISS/SIMS Data for 2024 Al Alloy UV/O_3 Cleaned.

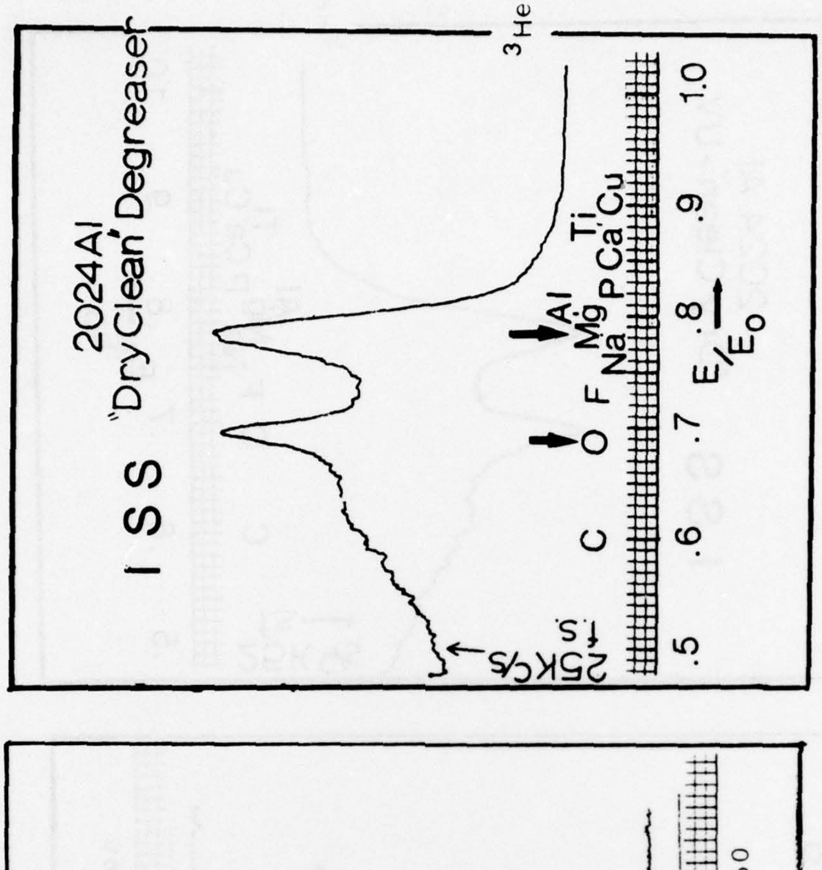

Figure 6. ISS/SIMS Data for 2024 Al Alloy Cleaned in a Commercial Degreaser.

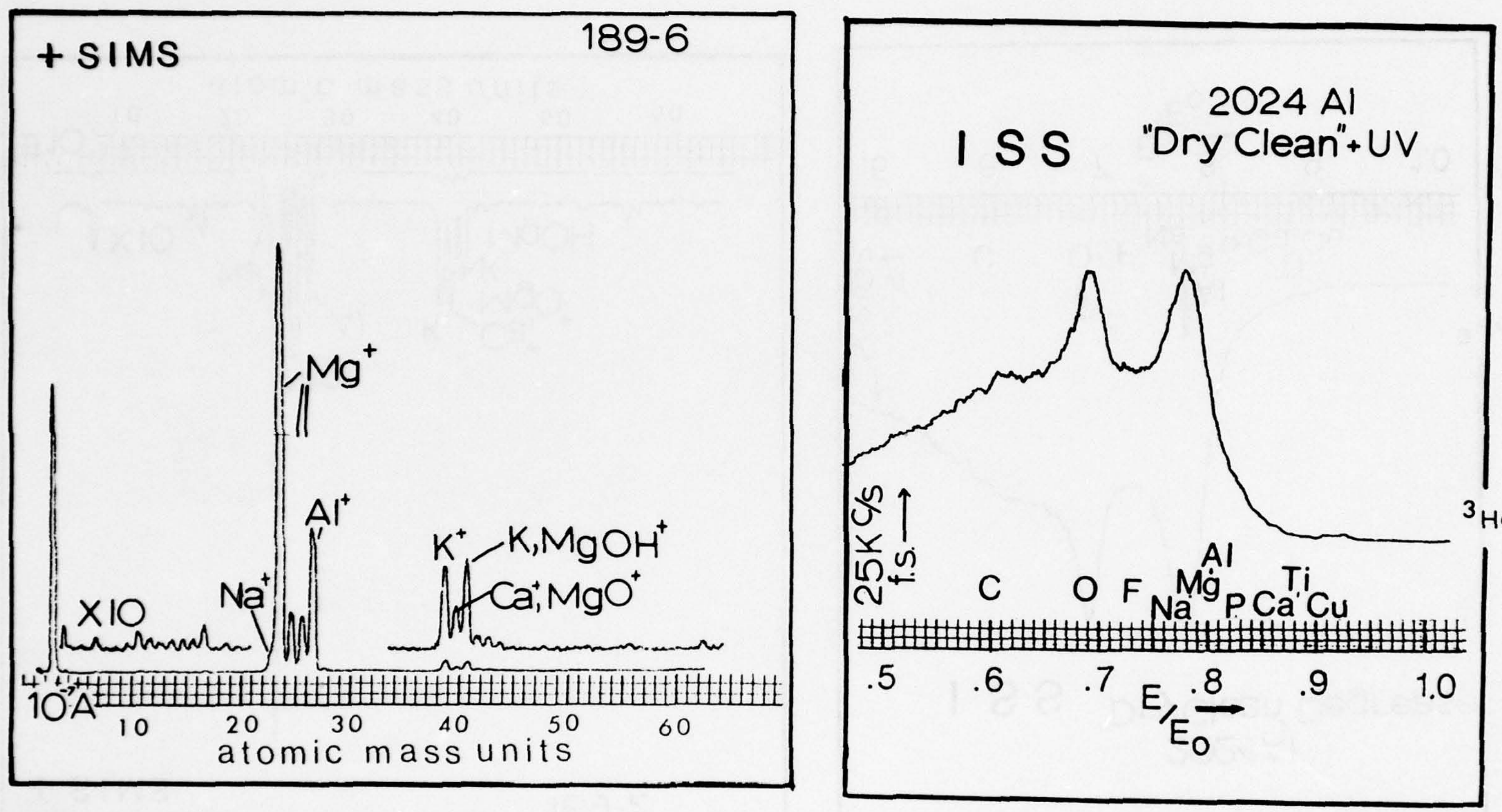

Figure 7. ISS/SIMS Data for 2024 Al Alloy Cleaned First in Degreasing Solution and then under UV/O_3.

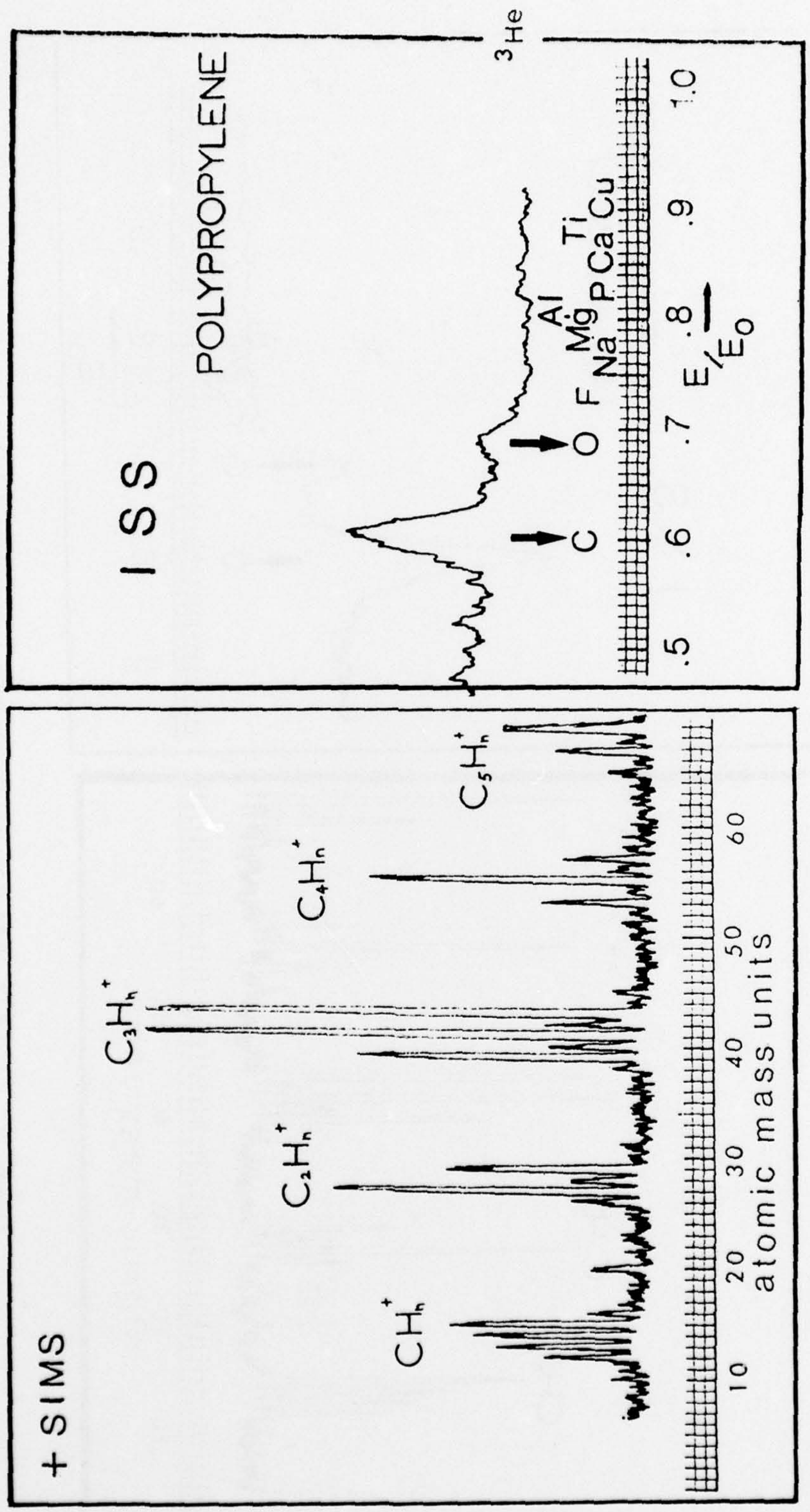

Figure 8. ISS/SIMS Data for Polypropylene.

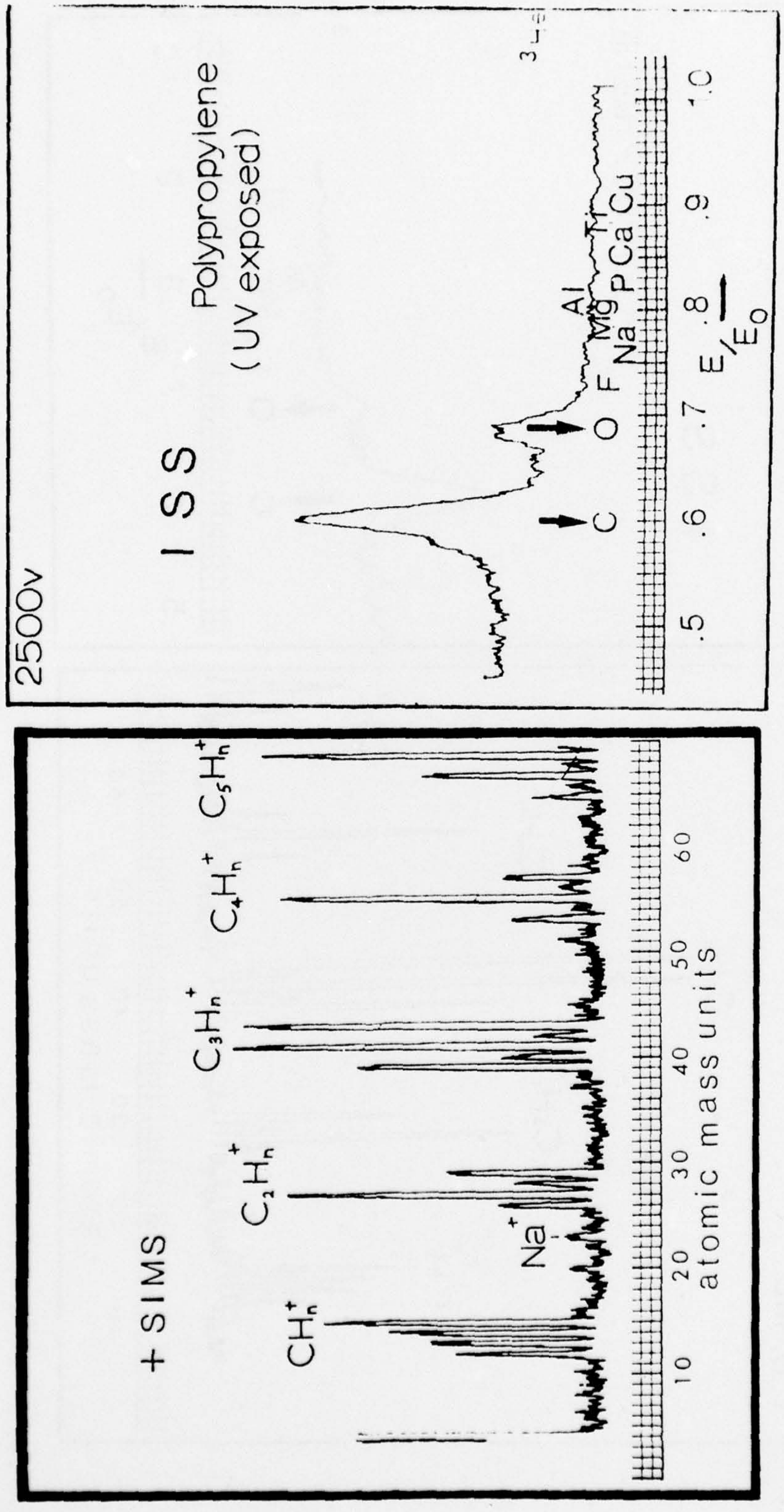

Figure 9. ISS/SIMS Data for Polypronylene Exposed to UV/O_3.

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